

**CLAIMS**

1. An apparatus for electrolytically treating a metal surface,  
comprising  
5 an electrochemical cell, wherein the electrochemical cell comprises  
an anodic chamber having an anode disposed therein, and  
containing a conductive anodic medium;  
a cathodic chamber containing the metal surface as a cathode, and  
containing a conductive cathodic medium comprising at least one silica-  
10 containing mineral composition; and  
a divider separating the conductive anodic medium from the  
conductive cathodic medium.
2. The apparatus of claim 1, wherein the treating comprises  
15 depositing a coating or film of a silicon-containing mineral by operation of the  
apparatus.
3. The apparatus of claim 1, wherein the conductive anodic medium  
has a pH of about 9 or higher.  
20
4. The apparatus of claim 1, wherein the conductive anodic medium is  
free of oxidizable organic or inorganic additives.
5. The apparatus of claim 1, wherein the conductive cathodic medium  
25 contains at least one organic or inorganic compound which would oxidize if in the  
anodic chamber.

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6. The apparatus of claim 5, wherein the at least one organic or inorganic compound remains substantially free of oxidation during operation of the apparatus.

5 7. The apparatus of claim 1, wherein the divider comprises at least one of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode-conforming ion-selective membrane and a porous ceramic.

10 8. The apparatus of claim 1, wherein the conductive cathodic medium further comprises a lubricant.

15 9. The apparatus of claim 8, wherein the lubricant comprises one or more of a polyethylene wax, PTFE, a hydrocarbon oil, a vegetable oil, a chlorinated paraffin, a phosphate ester, a sulfurized oil, a sulfurized fat, a poly- $\alpha$ -olefin, a polyglycol, and a carboxylic ester.

20 10. The apparatus of claim 1, wherein the anode comprises an active metal free of protection by a noble metal.

11. The apparatus of claim 1, wherein the anode comprises an uncoated active metal.

25 12. The apparatus of claim 1, wherein when the electrochemical cell is operated with an uncoated steel anode with applying an electric current at a constant potential across the electrochemical cell, substantially no loss of current flow is observed and substantially no anode residue is produced after 30 minutes.

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13. The apparatus of claim 1, wherein in operation of the apparatus the anode remains substantially free of accumulation of foreign materials.

5 14. The apparatus of claim 1, wherein in operation of the apparatus organic or inorganic compounds in the conductive cathodic medium remain substantially free of oxidation by oxygen generated at the anode.

15. The apparatus of claim 1, wherein the conductive cathodic medium comprises one or more of catechol, resorcinol and hydroxyquinone.

10 16. A process of treating a metal surface, comprising  
providing a metal surface;  
providing an electrochemical cell, wherein the electrochemical cell  
comprises:

15 an anodic chamber having an anode disposed therein, and  
containing a conductive anodic medium;  
a cathodic chamber containing the metal surface as a  
cathode, and containing a conductive cathodic medium comprising  
at least one silica-containing mineral composition; and  
20 a divider separating the conductive anodic medium from the  
conductive cathodic medium  
applying an electric current to the electrochemical cell at a rate and period  
of time sufficient for treating the metal surface.

25 17. The process of claim 16, wherein the treating comprises depositing  
a coating or film of a silicon-containing mineral.

18. The process of claim 16, wherein the conductive anodic medium  
has a basic pH.

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19. The process of claim 16, wherein the conductive anodic medium is free of oxidizable organic or inorganic additives.

20. The process of claim 16, wherein the conductive cathodic medium contains at least one organic or inorganic compound which would oxidize if in the anodic chamber.

21. The process of claim 16, wherein the divider comprises at least one of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode-conforming ion-selective membrane and a porous ceramic.

22. The process of claim 16, wherein the conductive cathodic medium further comprises a lubricant.

23. The process of claim 22, wherein the lubricant comprises one or more of a polyethylene wax, PTFE, a hydrocarbon oil, a vegetable oil, a chlorinated paraffin, a phosphate ester, a sulfurized oil, a sulfurized fat, a poly- $\alpha$ -olefin, a polyglycol, and a carboxylic ester.

24. The process of claim 16, wherein the anode comprises an active metal free of protection by a noble metal.

25. The process of claim 16, wherein the anode comprises an uncoated active metal.

26. The process of claim 16, wherein when the electrochemical cell is operated with an uncoated steel anode with the applying an electric current at a constant potential across the electrochemical cell, substantially no loss of current

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flow is observed and substantially no anode residue is produced after 30 minutes.

5           27.    The process of claim 16, wherein during the applying an electric current, the anode remains substantially free of accumulation of foreign materials.

10           28.    The process of claim 16, wherein during the applying an electric current, organic or inorganic compounds in the conductive cathodic medium remain substantially free of oxidation by oxygen generated at the anode.

15           29.    The process of claim 16, wherein the conductive cathodic medium comprises one or more of catechol, resorcinol and hydroxyquinone.